Environmental Pollution 195 (2014) 101–108

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Passive sampling of nonpolar contaminants at three deep-ocean sites

Kees Booij*, Ronald van Bommel, Hendrik M. van Aken, Hans van Haren, Geert-Jan A. Brummer, Herman Ridderinkhof

NIOZ Royal Netherlands Institute for Sea Research, P.O. Box 59, 1790 AB, Texel, The Netherlands

ARTICLE INFO

Article history:
Received 12 May 2014
Received in revised form
30 July 2014
Accepted 11 August 2014
Available online 7 September 2014

keywords:
Passive sampling
Nonpolar contaminants
Deep ocean
Performance reference compounds
Semipermeable membrane devices

ABSTRACT

Concentrations of polychlorinated biphenyls, polyaromatic hydrocarbons, hexachlorobenzene, and DDE were determined by passive sampling (semipermeable membrane devices) with exposure times of 1–1.5 years at 0.1–5 km depth in the Irminger Sea, the Canary Basin (both North Atlantic Ocean), and the Mozambique Channel (Indian Ocean). The dissipation of performance reference compounds revealed a pronounced effect of hydrostatic pressure on the sampler-water partition coefficients. Concentrations in the Irminger Sea were uniform over the entire water column (0.1–3 km). At the Canary Basin site, concentrations were 2–25 times lower near the bottom (5 km) than at 1.4 km. Concentrations in the Mozambique Channel (0.6–2.5 km) were lower than at the other two locations, and showed a near-bottom maximum. The data suggest that advection of surface waters down to a depth of about 1 km is an important mechanism of contaminant transport into the deep ocean.

1. Introduction

Little data is available to assess the role of the deep ocean in the global fate of organic contaminants. Transport models consider the water below the surface mixed layer to be unimportant for atmosphere-water and meridional transport of organics (Semeena and Lammel, 2003; Gouin and Wania, 2007). Transport from the surface mixed layer to the deep ocean by vertical advection and particle settling is generally considered to be small or negligible on the time scale of decades (Wania and Mackay, 1995; Gouin and Wania, 2007). By contrast, Gustafsson et al. (1997) argue that transport rates of polychlorinated biphenyls (PCBs) to the deep North Atlantic Ocean are larger than atmospheric photo-degradation rates of these compounds, and a modelling approach by Scheringer et al. (2004) suggested that deposition to the deep ocean retards the long range transport of the heavier PCBs. Lohmann et al. (2006) estimate that PCB transport by deep convection is more important locally than particle mediated transport in the Norwegian Sea, Labrador Sea, Weddell Sea, and Ross Sea.

Transport to the deep ocean has been demonstrated using sediment trap data (Knap et al., 1986; Gustafsson et al., 1997; Dachs et al., 1999; Bouloubassi et al., 2006). Dissolved and particulate PCBs have been determined using in situ filtration/extraction of deep waters in the North Atlantic Ocean, near the South-Western edge of the Porcupine Abyssal Plain (47 °N 20 °W) (Schulz et al., 1988). Similar measurements have been made for PCBs and PAHs around Iceland (Schulz-Bull et al., 1998). Passive sampling methods have been widely used for determining concentrations of freely dissolved nonpolar contaminants in surface waters (Stuer-Lauridsen, 2005; Greenwood et al., 2007; Allan et al., 2009), but not in the deep ocean. Lohmann and Muir (2010) recognised the potential of passive samplers for monitoring nonpolar contaminants around the globe, including the open ocean. The increased use of bottom landers and semi-permanent moorings for long-term monitoring of ocean current velocities, sedimentation, temperature, and salinity, among others, offers opportunities to collect contaminant concentration data in the deep ocean, at a small additional cost. Such data may be complementary to concentration data obtained by large-volume filtration/extraction methods. The latter methods are labour intensive, requiring the filtration and extraction of several hundred up to one thousand litres of water, and extreme care in controlling the blank levels (Schulz-Bull et al., 1998; Sobek and Gustafsson, 2004), but their application is not confined to specific mooring locations. Passive sampling methods are technically less complicated, but require attachment to a mooring or lander, and long exposure times are needed to extract sufficiently large volumes of water (400–1000 L), e.g., several months, up to one year, at equivalent water sampling rates of several litres per day. Further, passive samplers yield estimates of time-averaged concentrations of freely dissolved compounds,

* Corresponding author.
E-mail address: kees.booij@nioz.nl (K. Booij).

http://dx.doi.org/10.1016/j.envpol.2014.08.013
0269-7491/

whereas filtration extraction methods yield the instantaneous concentrations of freely dissolved plus colloidally bound compounds.

The aim of this study was to assess the potential of passive sampling to determine aqueous concentrations of nonpolar contaminants at deep ocean sites.

2. Methods

2.1. Passive samplers

Semipermeable membrane devices (SPMDs) were constructed using low-density polyethylene (LDPE) lay-flat tubing (2.54 cm wide, wall thickness 112 μm, Brentwood Plastics Inc., St. Louis, MO, USA) and triolein (99% purity, Sigma–Aldrich), following methods described previously (Booij et al., 2006). The SPMD dimensions were: length 64.9 ± 0.6 cm, mass 0.0039 ± 0.0001 kg, surface area 330 ± 3 cm^2. The triolein mass fraction was 0.166 ± 0.004, which is somewhat smaller than the recommended value of 0.20 (p. 186 of Huckins et al., 2006), but this only has a marginal effect (<11%) on the SPMD-water partition coefficients (Supplementary data, S1). The triolein was spiked with performance reference compounds (PRCs) prior to construction of the SPMDs: 410 ng g^{-1} acenaphthene–d_{10}, PCB4, phenanthrene–d_{10}, fluoranthene–d_{10}, and chrysene–d_{12}, and 15 ng g^{-1} PCB29, PCB155, and PCB204. After construction, SPMDs were stored at −20 °C in separate hexane rinsed glass jars with lids that were lined with hexane-rinsed aluminium foil.

Exposure cages consisted of 7 titanium rods (5 mm diameter), clamped between two poly(oxymethylene) plates (2 cm thickness) that also supported a titanium or anodised aluminium mesh screen (1.5 × 1.5 cm openings) (Supplementary data, S2).

Before each deployment cruise, the SPMDs were mounted in the cages at the laboratory, with the exception of the deployments in the Mozambique Channel, for which the samplers were mounted in the cages on board of the ship, for logistic reasons. The cages were wrapped in aluminium foil and transferred to 22 × 50 cm air tight tins that were transported to the ships on dry ice and kept at −20 °C shipboard. About one hour before deployment, the tins were brought on deck. Immediately before deployment, the tins were opened, the cages were mounted on the mooring cable with four bolts (Supplementary data, S2), and the aluminium foil wrappings were removed. Upon recovery of the mooring, the cages were removed from the cable, transferred to the tins, and stored at −20 °C, as quickly as possible (15–30 min), to minimise exposure to the atmosphere on deck. Field control samplers received the same treatment as the deployed samplers, except for the actual deployment. Fabrication control samplers were kept frozen in the laboratory.

After recovery, the surfaces of the SPMDs were cleaned with a damp paper tissue to remove the biofilm. Only a faint brown colour was visible on the paper tissues, indicating minimal fouling. Only one SPMD (Mozambique Channel, 100 m) was damaged during the exposures, showing that the samplers had sufficient strength for a 1 to 1.5 y exposure in the deep ocean. SPMDs were extracted twice (16 h + 24 h) with 200 mL pentane. Internal standards (PCB112, PCB198, anthracene-d_{10}, pyrene-d_{10}, benzo[*a*]anthracene-d_{12}, perylene-d_{12}, indeno[*1,2,3-cd*]pyrene-d_{12}) were added at the beginning of the first extraction. The concentrated extracts were cleaned-up with silica (2 g, deactivated with 6% water, elution with pentane), and were analysed by GC–ECD for HCB, 4,4′-DDE, PCBs) and by GC-MS for PCB4 and PAHs with 3–6 aromatic rings (Supplementary data, S4).

Recoveries, determined from spiked SPMDs, were 102 ± 12% for PAHs and 100 ± 9% for HCB/DDE/PCBs. Contaminant levels in the solvent blanks were 4 ng for phenanthrene, 0.2 ng for the other PAHs, and 0.04 ng for the chlorinated compounds. The amounts in the fabrication control samplers were higher: 11 ng for phenanthrene, 3 ng for fluoranthene, 1 ng for pyrene, 0.5 ng for the other PAHs, and 0.2 ng for the chlorinated compounds. Contaminant levels in the field control samplers were higher than in the fabrication controls by a factor of about 2 for the PAHs and the di-, tri-, and tetrachlorobiphenyls. No differences between field controls and fabrication controls were observed for DDE, HCB, and the higher chlorinated PCBs. Detection limits (LOD) were calculated as the average plus three times the standard deviation of the amounts that were detected in the field controls. The average amounts in the field controls were subtracted from the amounts detected in the exposed samplers. A comparison of amounts detected in solvent blanks, fabrication controls, field controls, and a typical exposed SPMD is given in the Supplementary data (S3).

SPMD-water partition coefficients in (K_{sw}) (L kg^{-1}) were calculated from

$$\log K_{sw} = 0.885 \log K_{PE-w} + 0.88 + K_s I \quad s = 0.17,\ R^2 = 0.98 \tag{1}$$

$$\log K_{sw} = 1.057 \log K_{ow} - 0.45 + K_s I \quad s = 0.30,\ R^2 = 0.95 \tag{2}$$

where $\log K_{PE-w}$ is the LDPE-water partition coefficient, K_s is the Setschenow constant (L mol^{-1}), used to adjust the partition coefficients for salinity, and I is the ionic strength of the water. These correlations were based on measured and calculated K_{sw} values as outlined in the Supplementary data (S5). Eq. (2) is less accurate (standard error of 0.30 vs. 0.17), but can be used when $\log K_{PE-w}$ is not available. A K_s value of 0.35 L mol^{-1} was adopted for all analytes (Jonker and Muijs, 2010).

It was assumed (and verified below; Section 3.1) that equilibrium was attained for all compounds with membrane-controlled uptake rates. Hence, only water boundary layer-controlled sampling rates need to be considered. These can be modelled as (Huckins et al., 2006; Booij and Smedes, 2010)

$$R_s = \beta_V V_m^{-0.39} \tag{3}$$

where V_m is the molar volume (reflecting compound-specific effects on R_s) and β_V is a site-specific parameter. Sampling rates (R_s) were obtained by unweighted nonlinear least squares estimation (Booij and Smedes, 2010) by fitting the retained PRC fractions (f) as a function of $K_{sw}V_m^{0.39}$.

$$f = \exp\left(-\frac{R_s\, t}{K_{sw} m_s}\right) = \exp\left(-\frac{\beta_V\, t}{K_{sw} V_m^{0.39} m_s}\right) \tag{4}$$

where m_s is the sampler mass and t is time. Aqueous concentrations (C_w) were calculated from the absorbed amounts (N) using

$$C_w = \frac{N}{K_{sw}\, m_s \left[1 - \exp\left(-\frac{R_s\, t}{K_{sw} m_s}\right)\right]} = \frac{N}{K_{sw}\, m_s \left[1 - \exp\left(-\frac{\beta_V\, t}{K_{sw} V_m^{0.39} m_s}\right)\right]} \tag{5}$$

Selected values of V_m and $\log K_{sw}$ are listed in the Supplementary data (S4).

2.2. Study area

Deployments were made in the Irminger sea (59.1 °N, 35.7 °W), the Canary Basin (29.4 °N, 23.1 °W), and the Mozambique Channel (16.7 °S, 40.9 °E), at depths of 0.1–5.1 km below the surface, for periods of 343–584 days in the years 2003–2005. Area map, bottom topography, horizontal and vertical positions of the samplers, deployment times, and average current velocities, temperatures, and salinities are summarised in the Supplementary data (S6, S7, S8).

3. Results and discussion

3.1. Sampling rate estimation

Analysis of the residuals in the modelling of PRC retention (Eq. (4)) revealed systematic deviations. The mean of the residuals for each PRC (averaged over all exposures) should not be significantly different from zero if Eq. (4) is a valid model for PRC retention and if the K_{sw} values are correct. Instead, the observed retained fractions of PCB29 and PCB155 were significantly smaller than the modelled fractions, whereas the reverse was true for acenaphthene–d_{10}, phenantrene–d_{10}, PCB4, fluoranthene–d_{10} (Fig. 1). Residuals (observed − modelled) for PCB29 were negatively correlated with exposure depth ($p < 0.01$, Fig. 2) and positive correlations with depth were found for acenaphthene-d_{10}, phenanthrene-d_{10}, and fluoranthene-d_{10} ($p < 0.001$) (Supplementary data, S9).

The origin of the depth dependency of the residuals is illustrated in Fig. 3 for the shallowest (0.1 km) and deepest (5.1 km) exposure site. Retention data for PCBs and PAHs follow distinct model lines, which are close together for shallow exposures but are increasingly separated at greater depth. When PCB and PAH data are modelled together (solid lines in Fig. 3), the difference between observed and modelled PCB29 retention increases from 0.1 at 100 m to 0.3 at 5.1 km. Because the uptake rates of PCBs and PAHs are controlled by the water boundary layer it is unlikely that these compound groups actually have different sampling rates. We therefore suggest that the differences in PRC retention as a function of $\log K_{ow}$ are caused by inaccuracies in the K_{sw} values of these compound groups. These differences cannot be explained by temperature differences between shallow (~11 °C) and deep waters (~1 °C). Booij et al. (2003) found no measureable effect of temperature on the K_{sw} of SPMDs for PAHs, hexachlorobenzene, and PCBs. Huckins et al. (2002) reported a 0.2 log units decrease in the K_{sw} per 10 °C temperature increase for phenanthrene, but not for PCB52 and 4,4′-DDE. The shift of the model curve for PCBs relative to PAHs (~0.8 log units, Fig. 3 right) is much larger than can be explained by temperature. We therefore hypothesize that these effects are mainly caused by